

Review Article

Fluoride Sorption Properties of Plant Biomass: Unveiling Inconsistency in the Past Three Decades

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Abstract

The high cost of advanced technology for defluoridation has, since the late 20th century, triggered the search for low-cost water defluoridation methods. One such effort involves the use of plant biomass materials. Over the past thirty years, our understanding of fluoride sorption mechanisms of non-activated plant biomass has not significantly advanced, partly due to inconsistencies and incompleteness of defluoridation studies. This research aimed at investigating how inconsistencies and incomplete selections of study parameters have impacted our understanding of key defluoridation properties of non-activated plant biomass materials, specifically fluoride sorption mechanisms. The study reviewed 37 studies that explored the application of non-activated plant biomass in water defluoridation, comparing methods and findings while identifying reasons for deficits. Findings revealed significant inconsistencies and incompleteness in the selection of study parameters, leading to unsubstantiated proposals for plausible sorption mechanisms. This has deprived the research community of a thorough understanding despite thirty years of studies in the field. This study, therefore, concludes that selection study parameters is a crucial component in enhancing our understanding of fluoride sorption properties of plant biomass materials. For an in-depth understanding of fluoride sorption mechanisms, this study identified three crucial parameters that must be included in future studies: the effect of pH variation, the point of zero charge of the adsorbent, and FT-IR spectral shifts.

Keywords

FT-IR Spectral Shifts, Point of Zero Charge, Fluoride Sorption, Non-activated Plant Biomass, Study Parameters

1. Introduction

The presence of fluoride in water is associated with the occurrence of fluorosis in communities within affected areas. The application of advanced defluoridation techniques is limited due to their high cost. Therefore, the low cost and renewability of plant biomass materials substantiate their potential for wide application in water defluoridation, especially in the developing world, where point-of-use application is recommended. However, field application of any material is

possible only when their defluoridation properties are well understood. Selection of parameters is central to understanding the defluoridation properties of plant biomass materials. Yet, three decades of using non-activated plant biomass for water defluoridation reveal inconsistencies in parameter selection, hindering the understanding of fluoride removal mechanisms. For instance, early studies on water defluoridation by plant biomass included only three parameters (solution

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Received: 8 February 2025; **Accepted:** 3 March 2025; **Published:** 18 March 2025



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pH, contact time, and particle size) [1]. More parameters were later added for Aloe and Tamarind seed biomass studies, such as particle size, surface characteristics, solution temperature, contact time, initial fluoride concentration, adsorbent dose, solution pH, and point of zero charge [2, 3]. The proposed fluoride removal mechanism involved electrostatic interactions, based on the effect of solution pH and point of zero charge values. Variation in solution pH affected fluoride removal efficiency, with the highest removal at pH below the point of zero charge, indicating the role of electrostatic forces.

In subsequent studies, Yadav et al. [4] included solution pH, adsorbent dose, contact time, and initial fluoride concentration, predicting chemical interactions from kinetic models. The varying fluoride removal efficiency of sawdust and wheat straw suggested surface charge significantly impacted the process, but the point of zero charge was not determined. Paradelo et al. [5] studied adsorbent pH, solution pH, initial fluoride concentration, and contact time for pine bark biomass, suggesting fluoride removal based on surface charges, though without determining the point of zero charge. Keshtkar et al. [6] studied *Syzygium cumini* and *Prosopis cineraria* leaf biomass, including point of zero charge, surface morphology, contact time, and initial fluoride concentration, proposing interaction mechanisms based on kinetic models but omitting the effect of solution pH. An examination of these studies reveals significant inconsistencies in the selection of parameters.

This study critically reviews water defluoridation studies by plant biomass to highlight the effect of inconsistency in parameter selection and identify key parameters for understanding fluoride removal mechanisms. This approach aims to shape and direct future research and contribute to the real-life application of these materials for water defluoridation. It is envisaged that findings from this study will accelerate our understanding of the functional groups responsible for fluoride sorption and the mechanisms involved in plant biomass materials, thus expediting the practical application of these materials.

2. Materials and Methods

The Papers presenting the use of plant biomass materials in water defluoridation were retrieved through different search engines from the World Wide Web (www) including Google scholar, Scopus and Web of Science by using the following search terms: “plant biomass for fluoride removal”, “fluoride removal by plant biomass”, “water defluoridation by plant biomass”, “fluoride sorption” and “fluoride removal by low cost biosorbents”. Many retrievable studies on water defluoridation by plant biomass could be found dating from early 21st century. Therefore, the search for relevant literature was extended to 1990s during which two studies could be retrieved one in 1991 and the other in 1998. This makes the 37 publications used in this study cover the period from 1991 to 2021. Although greater than this number of publications could be

retrieved, the focus was on articles that presented the defluoridation properties of non-activated plant biomass materials. Thus, when a retrieved publication included both the non-activated and activated plant biomass materials, only results from the non-activated plant biomass materials were used.

In the review process, the history of and trends in the water defluoridation by non-activated plant biomass were summarised and the general motivation for selection of such materials identified. Using the effect of solution pH on fluoride removal efficiency, different plant biomass materials were divided into two categories based on their response to variation of solution pH. The variation in the studied parameters in the different studies throughout history was critically studied. The relationship between the studied parameters and the proposed fluoride removal mechanisms were established and lessons drawn. The lessons drawn from the studied parameters related to the proposed mechanisms were used to propose the “must include” parameters in the future studies for better understanding of the plausible fluoride removal mechanisms by non-activated plant biomass materials.

3. Results and Discussion

3.1. The History of Water Defluoridation by Non-Activated Plant Biomass

Published studies on water defluoridation by plant biomass started to appear in the late 20th century [1, 7]. The motivation was to present a low cost and eco-friendly material for water defluoridation (Table 1). The defluoridation capacities of the two studied plant biomass, duckweed (*Spirodela polyrrhiza*) and nirmali (*Strychnos potatorium*) seeds were found to be relatively low, namely, 0.91 and 0.15 mg/g respectively. However, the difference in sorption capacities revealed that different plant biomass materials have different water defluoridation properties. This triggered expanded studies on both the non-activated and the activated plant biomass in the early 21st century which demonstrated further from varied individual studies that different plant biomass materials have different defluoridation properties [2, 3, 8-10]. Therefore, further studies in the second decade of the 21st century on fluoride removal properties of plant biomasses involved a comparison of defluoridation properties of different plant biomass materials under similar conditions [4, 6, 11-14]. From these studies, it could be confirmed that different biomass materials have different fluoride removal properties. From early 21st century, efforts to understand the fluoride removal mechanism by plant biomass materials were intensified [2, 3] and biomass material properties such as point of zero charge and pH of the treated water were related to the fluoride removal efficiencies. Upon examination on the methods used in these studies, a great variation in selection of studied parameters could clearly be seen. This could affect the authenticity of the proposed fluoride sorption mechanisms in

those studies and retard our understanding of properties of these materials. In the next section, the studied parameters are

identified and their relations to the defluoridation properties are highlighted.

Table 1. A summary of the selected plant biomass materials used for water defluoridation and motivation(s) for their selection.

Biomass type(s)	Motivation(s)
Duck weed (<i>Spirodela polyrrhiza</i>)	Low cost materials
Nirmali seeds	Other application/low cost materials
Water hyacinth (<i>Eichhornia crassipe</i>)	Low cost materials
Neem (<i>Azadirachta indica</i>) leaves	
Pipal (<i>Ficus religiosa</i>) leaves	
Khair (<i>Acacia catechu wild</i>)	Low cost materials
Tamarind seed	Waste re-use/low cost materials

3.2. Fluoride Sorption Properties of Different Plant Biomass: Parameters, Efficiency and Mechanisms

Srimurali et al. [1] examined the defluoridation properties of both activated and non-activated nirmali (*Strychnos potatorum*) seeds. The non-activated biomass demonstrated a fluoride sorption efficiency of 5.9% at a dose of 2 g/L, an initial fluoride concentration of 5 mg/L, and neutral pH. Due to its low fluoride removal efficiency, only the activated form was further studied, leaving the causes of the low efficiency unexplored. Murugan and Subramanian [2] expanded parameters in their study of Indian Aloe vera, including the point of zero charge (pzc), solution pH, and initial fluoride concentration. A defluoridation capacity of 4.41 mg/g at neutral conditions, with the pzc influencing surface charge and fluoride trapping efficiency was found. These results suggest multiple fluoride removal mechanisms. Sinha et al. [8] reported low fluoride removal efficiency for non-activated water hyacinth and the reasons for low sorption were not explored, neither the fluoride removal mechanism. Using findings from Murugan and Subramanian [2], published a year before Sinha et al's [8] study, the impact of pH and pzc could be revisited to predict interactions between fluoride ions and biomass surface.

Jamode et al. [5] found neem, pipal, and khair had 80% defluoridation efficiency at pH 2. The proposed mechanism was based on kinetic models, but determining the pzc would provide a more comprehensive understanding. Murugan and Subramanian [3] found tamarind seed biomass had a pzc of 7.44 and a defluoridation capacity of 6.09 mg/g at neutral pH. The optimal pH for fluoride removal was 7, suggesting Coulombic forces between fluoride ions and biomass surface. Functional group analysis would enhance understanding of

active sites and thence, sorption mechanisms. Parmar et al. [10] noted low fluoride removal efficiency for non-activated corn cob biomass, forsaking further exploration to identify causes for low sorption, thence, denying understanding of the mechanisms involved.

Lakshminarayan et al. [15] reported defluoridation properties of neem and pipal leaf biomasses. 30% fluoride removal efficiency at neutral pH was reported. However, the surface charge and sorption mechanisms were not explored. Vardhan and Karthikeyan [11] found Moringa seed biomass had higher fluoride removal efficiency (87%) compared to rice husk (84%) at pH 6. Results showed that pH significantly influenced fluoride removal efficiency, suggesting appropriate selection of pH for comparison as an important parameter. The pzc determination would clarify surface charge effects. Yadav et al. [4] found Indian rosewood and wheat straw had different defluoridation efficiencies, with wheat straw showing higher efficiency at pH 8 and rosewood at pH 2. The pzc, which was not determined, would help in understanding the influence of pH on surface charge and fluoride sorption mechanisms.

These studies highlight the fragmented nature of research on plant biomass defluoridation, emphasizing the need for consistent selection of key parameters to better understand the interactions between fluoride ions and biomass surfaces. *Tinospora cordifolia* studied by Pandey et al. [21], using an adsorbent particle size of 18 microns was found to have the maximum fluoride removal efficiency of 70% at the dose of 7 g/L and initial fluoride concentration of 5 mg/L. The studied parameters included the effect of initial fluoride concentration, adsorbent dose, adsorbent surface characteristics, FT-IR spectral shift, contact time, solution pH and co-ions. For this biomass material, an increase in pH was found to cause a decrease in fluoride removal efficiency. However, pH 7 gave an exceptionally higher fluoride removal efficiency in the

studied pH range (3-8). The proposed mechanism was a substitution reaction between the fluoride in the water and the amine groups on the biomass surface. This proposal was based on the FT-IR spectral shift in the amine groups. However, the decline in fluoride removal efficiency with increasing pH could suggest that pH induced surface charges affect the fluoride sorption. The FT-IR spectral shift readings coupled with the effect of solution pH on fluoride removal efficiency and the point of zero charge values could give more complete insights on the type of interactions between the adsorbent and fluoride ion and the active sites involved, thence, the possible fluoride removal mechanism.

Harikumar et al. [12] compared the defluoridation properties of six biomass materials: vetiver, tamarind seed, clove, neem, acacia, nutmeg, and coffee husks. Their defluoridation efficiencies were 75%, 70%, 52%, 47%, 45%, and 38%, respectively, at pH 6. Parameters studied included the effect of adsorbent dose, particle size, contact time, biomass type, solution pH, and surface morphology. The fluoride removal mechanism was proposed to be adsorption and inter-particle bridging. The type of adsorption could be better understood using point of zero charge values to explain trends in solution pH.

Kumar et al. [22] studied the defluoridation properties of tamarind fruit cover with over 70% efficiency at a dose of 5 g/L, fluoride concentration of 10 mg/L, and pH of 6. The parameters included the effect of adsorbent surface morphology, solution pH, co-ions, and adsorbent dose. The fluoride removal mechanism proposed was adsorption influenced by charge interactions. However, predicting the surface charge was challenging without point of zero charge values. Balouch et al. [23] found 80% fluoride removal efficiency when sawdust was used at an initial fluoride concentration of 5 mg/L, a dose of 20 g/L, and pH 6. Parameters included point of zero charge, the effect of contact time, agitation speed, solution pH, and adsorbent dose. Fluoride removal increased with pH up to the optimal pH of 6, which is higher than materials' point of zero charge value of 4.9, indicating multiple interactions additional to electrostatic forces.

Patil et al. [13] compared five biomass materials and found fluoride removal efficiency decreased with increasing pH. Parameters included the effect of solution pH, contact time, adsorbent dose, initial fluoride concentration, temperature, particle size, and agitation speed. The fluoride removal mechanism was not proposed but could be better understood with point of zero charge values. Sumalatha et al. [24] reported 90% fluoride removal efficiency for *Citrus limonium* biomass at an initial fluoride concentration of 5 mg/L, a dose of 16.67 g/L, and pH 6. Parameters included the effect of contact time, adsorbent dose, particle size, and initial fluoride concentration. The fluoride removal mechanism was not proposed, though previous studies highlighted the correlation between solution pH and fluoride adsorption efficiency. Mwakabona et al. [14] found different biomass materials had varying fluoride removal efficiencies: sisal pith (47.3%), *Aloe*

vera (29.4%), sisal fiber (7.1%), banana pseudo stem (4.6%), goose grass (4.1%), and maize leaf biomass. Parameters included contact time, adsorbent dose, solution pH, initial fluoride concentration, and biomass type. The fluoride removal mechanism was proposed to be electrostatic interactions. However, predicting surface charge without point of zero charge values is difficult.

Bharali and Bhattacharyya [25] reported 82% fluoride removal efficiency for neem leaf biomass at an initial fluoride concentration of 3 mg/L, a dose of 5 g/L, and pH 6.8. Parameters included the effect of solution pH, anion exchange, contact time, adsorbent dose, surface characteristics, and temperature. The proposed fluoride removal mechanism was electrostatic interactions linked to surface protonation and deprotonation at varying solution pH. However, the effect of varying pH alone cannot be used to suggest involvement of charges in interaction. Paradelo et al. [5] found pine bark had 5.8% efficiency at an initial fluoride concentration of 2.5 mM, a dose of 1.11 g/L, and pH 7. Parameters included initial fluoride concentration, solution pH, biomass pH, and contact time. The proposed mechanism was electrostatic interactions, but predicting adsorbent surface charge based on the effect of solution pH alone without point of zero charge values is inadequate as established in the next section.

These studies highlight the variability and complexity of fluoride removal by plant biomass materials and underscore the need for consistent inclusion of key parameters like point of zero charge to better understand the interactions between fluoride ions and biomass surfaces. Banana (*Musa acuminata*) peel biomass, as used by Mondal [17], had a fluoride sorption efficiency of 90% at an initial fluoride concentration of 30 mg/L, a dose of 15 g/L, and pH of 4. The study parameters included the adsorbent point of zero charge, solution pH, adsorbent surface morphology and characteristics, initial fluoride concentration, adsorbent dose, contact time, co-ions, and temperature. The point of zero charge of the material was found to be 5.63 ± 0.05 . The fluoride removal efficiency of the biomass increased with increasing pH from 2-4, beyond which it steadily declined. The optimal solution pH for highest fluoride removal was below the point of zero charge value. The proposed fluoride removal mechanism involved electrostatic interactions between the negatively charged fluoride ions and the positively charged biomass surface. At neutral pH, fluoride removal was 75%. Using the reported point of zero charge, the biomass surface would be negatively charged at neutral pH, suggesting that other fluoride removal mechanisms besides electrostatic interactions may be involved [26]. Studying the FT-IR spectral shifts would help in understanding the fluoride sorption mechanisms involved.

Saikia et al. [18] demonstrated the defluoridation properties of possotia (*Vitex negundo*) leaf. The fluoride sorption efficiency was greater than 70% at an initial fluoride concentration of 3 mg/L, a dose of 3 g/L, and pH 8. Deviations from this optimal pH decreased efficiency. Parameters studied included cation exchange capacity, anion exchange capacity, contact

time, adsorbent dose, solution pH, and surface characteristics. The anion exchange capacity was higher than the cation exchange capacity, suggesting a higher affinity for anions. The lower fluoride removal below and above optimal pH was linked to hydrofluoric acid formation and hydroxyl ion competition. Point of zero charge would aid in predicting the surface charge at pH 8, contributing to ion exchange mechanisms. Romar-Gasalla et al. [27] investigated wheat straw with a fluoride removal efficiency of 93% at an initial fluoride concentration of 3 mg/L and pH 8. The point of zero charge was 6.68, indicating a negatively charged surface at pH 8. The proposed mechanism involved hydrogen bonds and van der Waals forces, suggesting reversible interactions.

Indian sandalwood (*Santalum album*) showed a fluoride removal efficiency of 75.7% at an initial concentration of 15 mg/L and pH 6.8 [19]. Parameters studied included solution pH, surface characteristics, temperature, contact time, and adsorbent dose. The proposed ionic interactions would be better understood with the point of zero charge value, which is often overlooked in studies predicting surface charge based solely on the effect of solution pH. George and Tembhurkar [20] found *Ficus glomerata* bark had a fluoride sorption capacity of 2.27 mg/g at neutral pH. The mechanism was proposed as chemisorption, but the absence of point of zero charge value and surface functional groups makes the prediction unsubstantiated. Sunitha and Reddy [28] reported Mint (*Mentha longifolia*) leaves had a 90% fluoride removal at an initial fluoride concentration of 10 mg/L and pH 5-6. The effect of solution pH was not reported, and the mechanism was not proposed.

Gandhi and Sirisha [29] reported *Passiflora foetida* fruits paste with a 95% fluoride removal efficiency at an initial fluoride concentration of 4 mg/L and pH 4-5. The proposed mechanism involved electrostatic interactions, which would be more informative with point of zero charge values determined. Keshtkar et al. [6] compared *Syzygium cumini* and *Prosopis cineraria* leaves, with defluoridation capacities of 11.52 mg/g and 7.407 mg/g, respectively. Point of zero charge values alone cannot correctly predict interaction involved. These studies confirm that water defluoridation research by plant biomass materials is fragmented. Key parameters for better understanding of interactions between fluoride ions and biomass surfaces are yet to be set. These could be set by extracting lessons learnt from findings reported in the past three decades as explained in the subsequent sections.

4. Discussion

4.1. Lessons from Studying the Effect of Varying Solution pH

From the previous sections, it is evident that solution pH is an important parameter when studying sorption properties

plant biomass materials. This is because findings showed strong correlation between pH variation and fluoride removal efficiency [2-4, 9, 11, 12, 14, 17-19, 22, 24, 30]. Based on the effect of pH variation on the fluoride removal efficiency, biomass materials can be categorized into two major groups (Table 3). The first group constitutes plant biomass materials with their fluoride removal efficiency declining steadily with increased solution pH. In the list are Neem leaves, Rice husks and Indian rosewood saw dust [4, 9, 11, 31]. The point of zero charge values of rice husk and neem leaves biomasses are 6.45 and 4 respectively, as reported in other related studies [32, 33]. This could suggest that the electrostatic forces play a major role in the interaction between the fluoride ion and the biomass materials because the highest removal efficiency is at the solution pH below the point of zero charge values. However, the steady decrease before and after the point of zero charge makes the former implication unsubstantiated.

Another group constitutes plant biomass materials with fluoride removal efficiency increasing with increasing pH to the optimal pH after which it declines with further increase in solution pH. Some examples in the list are wheat straw, banana peel, *Aloe vera*, *Tinospora cordifolia* leaves, Tamarind seed, *Azadirachta indica* leaves, pososia leaves, Indian sandalwood leaves, saw dust and *Passiflora foetida* fruits [2-4, 12, 17]. While some of these biomass materials have a higher fluoride removal efficiency at solution pH below the point of zero charge values [2, 3, 17] others show higher fluoride removal at solution pH above the point of zero charge values [23, 27]. This would imply that some other forces than electrostatic forces play a role in the fluoride-biomass interactions. This fact can be explained by the influence of the solution pH on the biomass surface charge as follows; increasing the solution pH decreases the pH induced charge on the surface of the biomass materials, thence, decreased charge dependent interactions between the negatively charge fluoride ion and the positively charged biomass surface. Therefore, the parallel increase of the fluoride removal efficiency and solution pH could be explained by the stability of the biomass active sites in acidic conditions.

Considering the condition of the targeted fluoride contaminated water, either group one or group two biomass materials could be selected (Table 3). Thus, determination of the effect of solution pH may be one of the key parameters which when determined the type of biomass and possible interactions with fluoride ion can be identified. However, the biomass materials that work best in the neutral condition are more likely to find way to field application in the treatment of the natural contaminated fluoride water. This calls for the need to purposively select those biomass materials that will give higher optimal pH for further study. One tool that would aid in such selection is the predetermination of the point of zero charge of the adsorbent as is further explained in the next section.

Table 2. A summary of scientific bases for proposed fluoride removal mechanisms of the selected plant biomass materials in relation to the studied parameters and their deficiencies.

Biomass	F removal mechanism(s)	Basis for proposing the mechanisms	Studied parameters	Deficiency	References
Aloe vera	Chemical forces	Effect of solution pH on the fluoride removal efficiency and the point of zero charge value of the biomass	Effect of (pH, initial F, dose and time), point of zero charge	Possible active sites not identified (FT-IR spectral shifts not determined)	[2]
Tamarind seed	Electrostatic forces	Optimal pH and point of zero charge value of the biomass	Effect of (pH, initial F, dose and time), point of zero charge	Possible active sites not identified (FT-IR spectral shifts not determined)	[3]
Tinospora cordifolia	Substitution reaction/ion exchange	FT-IR spectral shift	Effect of (pH, initial F, time and dose), FT-IR analysis before and after biomass use	Possible effect of surface charge not considered in the mechanism (point of zero charge not determined)	[21]
Dalbergia sissoo	adsorption	Effect of solution pH on the fluoride removal efficiency	Effect of (pH, time, dose and initial F)	Possible active sites & effect of surface charge not identified (FT-IR spectral shifts & point of zero charge not determined)	[21]
Musa acuminata	physisorption (electrostatic forces)	Effect of solution pH and point of zero charge value of the biomass	Effect of (pH, initial F, dose, co-ions, temperature and time), point of zero charge, SEM and FT-IR spectral shift	Nil	[17]
Santalum album	Ionic interactions	Types of functional groups present	Effect of (pH, initial F, dose, co-ions, temperature and time), SEM and FT-IR before use	Possible effect of surface charge not substantiated (point of zero charge not determined) Involved active sites not confirmable (FT-IR analysis after use not included)	[19]
Prosopis cineraria Syzygium cumini	Coulombic forces	Point of zero charge values and types of surface functional groups	Effect of (dose, time, initial F), XRD, FT-IR, SEM and point of zero charge values	Presence of coulombic forces not confirmable (effect of pH /optimal pH not determined) Involved active sites not predicted (FT-IR analysis after use not determined)	[6]

4.2. Lessons from Studying the Point of Zero Charge Values

Since the effect of the solution pH is one of the important parameters in understanding the fluoride removal properties of the biomass materials, it follows that, the point of zero charge value of the adsorbent is an equally important parameter to understand the possible defluoridation mechanisms of the studied plant biomass material (Table 4). A reflection on the reviewed studies reveals that only a small fraction of studies [2, 3, 16, 17, 23] included determination of both the point of zero charge and the effect of solution pH when studying the water defluoridation properties of their selected biomass materials. In most cases the pH at which the fluoride removal is highest was found to be

below the biomass's point of zero charge value [2, 3, 17]. Therefore, electrostatic interactions could be proposed as the major cause for the interaction between the fluoride ion and the biomass surface. However, this argument fits best the first group of biomass materials in which the fluoride removal efficiency declines steadily with increasing solution pH [4, 9, 11]. For the second group of biomass materials, where the increase in solution pH results in the increase in the fluoride removal efficiency, the use of point of zero charge value in predicting the nature of interaction between the fluoride ion and the biomass surface could not be validated especially when maximum removal efficiency is at pH higher than the pzc. Therefore, even though the point of zero charge is a useful tool in predicting the biomass surface charge and thus, possible interactions with the negatively charge fluoride ions, it is not the sole parameter. Keshtikar et al.

[6] showed a positive correlation between the point of zero charge and fluoride sorption capacity of the two biomass materials. *Syzygium cumini* biomass with pzc value of 5.2 had higher fluoride sorption capacity of 11.52 mg/g when compared to

Prosopis cineraria biomass with pzc of 4.4 and fluoride sorption capacity of 7.407 mg/g at neutral pH. This would suggest that at neutral pH the biomass material with lower pzc would be highly negatively charged than the other.

Table 3. Categorisation of plant biomass materials based on their fluoride removal efficiency in response to change in solution pH.

Material(s)	Category	Characteristics	Examples	References
Plant biomass	Group 1	F removal decreases with increasing solution pH	Saw dust, rice husks, Indian rosewood and Neem leaves,	[4, 9, 11, 23]
	Group 2	F removal increases with increasing solution pH	Tamarind seed, <i>Aloe vera</i> , Wheat straw, <i>Ti-nospora cordifolia</i> and Banana peel,	[2-4, 17, 21, 23, 27]

A similar positive correlation could be deduced from a study involving comparison of fluoride removal efficiencies of rice husk and Moringa seed biomass by Vardhan and Karthikeyan [11] which reported that at similar pH of 6, the fluoride sorption efficiency of Moringa seed biomass was greater (87%) than that of that of rice husk biomass (84%). The point of zero charge values of *Moringa oleifera* seed and rice husks biomasses reported in related studies reveal that, Moringa seed biomass (efficiency 87%) had higher point of zero charge value of 7.0 than rice husk (efficiency 84%) with point of zero charge of 6.45 [11, 31, 32]. Tamarind seed, neem leaves, and coffee husk biomass materials studied by Harikumar et al. [12] under similar conditions had the fluoride sorption efficiency of 75, 52, and 38%,

respectively, at pH 6. The point of zero charge values reported in other related studies are 7.44, 4, and 4.3-4.5 for tamarind seed, neem, acacia and coffee husk biomasses respectively [3, 33]. Similarly, *Aloe vera*, sisal fibre, banana pseudo-stem and maize leaf biomass materials were found to have the fluoride sorption efficiency of 29.4, 26.6, 7.1, and 4.1% respectively at pH 6 [14]. The point of zero charge values reported by related studies for these biomass materials are 7.43, 6, 5.5 and 5.1 for *Aloe vera*, sisal fibre, banana pseudo-stem and maize leaf biomass materials respectively [2, 34-36]. From these observed trends, the point of zero charge value could be used in predicting the fluoride removal efficiency of the selected biomass materials with limitations.

Table 4. Summary of the relationship between the point of zero charge values, optimal solution pH and F removal mechanisms of different plant biomass materials.

Biomass	Point of zero charge	Optimal pH	F removal mechanism	References
Aloe vera	7.43	7 (below pzc)	Chemical forces	[2]
Tamarind seed	7.44	7 (below pzc)	Electrostatic forces	[3]
Saw dust	4.9	6 (above pzc)	-	[26]
Banana peel	5.63	4 (below pzc)	Electrostatic forces	[17]
Wheat straw	6.8	8 (above pzc)	Van der Waals forces	[34]
<i>Syzygium cumini</i>	5.2	-	Electrostatic forces	[6]
<i>Prosopis cineraria</i>	4.4	-	Electrostatic forces	[6]

4.3. Lesson from the Proposed Fluoride Ion - Adsorbent Interaction Mechanisms

Understanding the reaction mechanisms between the fluoride ion contaminant and the adsorbent is important for properly

directed further studies and field application of such biosorbents. As pointed in the previous sections, while some studies propose the fluoride removal mechanism using the adsorbent surface characteristics and influence of the pH on the same, others base their proposal on kinetic models and energy studies [2, 3, 5, 6, 12, 14, 17, 23, 34]. However, at the core, it is biosorbent character-

istics that count. Therefore, highlighting the relationship between the adsorbent surface chemistry and related characteristics is important in studying the fluoride removal mechanisms [2-5, 11, 14, 17, 23, 34]. This, therefore, implies that subsequent studies employ a careful approach that aim at relating such parameters. A few studies use the point of zero charge values alone to propose the fluoride sorption mechanisms [2, 3, 17, 34]. Therefore, since it is well established that the solution pH will result into the positively charged surface only when it is less than the point of zero charge of the adsorbent [37], combining both parameters would generate more meaningful information. However, higher fluoride sorption properties at pH above the point of zero charge would suggest that other factors count in predicting the plausible sorption mechanisms. The FT-IR spectral shift reading which was used by some authors to propose the fluoride sorption mechanisms [21] is an additional parameter that is important in understanding the fluoride ion-biomass interactions. Coupling this with the point of zero charge values and the effect of the solution pH, the fluoride removal mechanisms can better be understood. It can thus be stated that predicting the fluoride sorption mechanism of the biomass based on either one of the parameters in absence of others is a presentation of incomplete information and may be misleading. Therefore, the adsorbent point of zero charge, effect of solution pH and biomass surface functional group before and after sorption are three key parameters to be included in the study for better understanding of the fluoride removal mechanisms involved.

5. Conclusions

In this study, the trend and challenges related to selection of study parameters in studying the water defluoridation properties of the non-activated plant biomass materials are identified and discussed. The parameters widely studied in the investigation of the defluoridation properties of the non-activated plant biomass include, adsorbent and adsorbate dose, contact time, solution pH and temperature with a significant variation of the number of parameters included in individual studies. Findings revealed that, in the studies conducted in the past 30 years since 1991, selection of study parameters has been inconsistent and incomplete presenting a significant setback in our understanding of fluoride sorption mechanisms of plant biomass materials. This study, therefore, proposes the inclusion of three study parameters, namely, solution pH, point of zero charge and FT-IR spectral shift as key parameters to understanding fluoride sorption mechanisms involved in future studies. Incorporating these parameters in future studies would assist in rapid growth of knowledge on functional groups and fluoride sorption mechanisms involved when non-activated plant biomass materials are used for water defluoridation.

Abbreviations

FT-IR Fourier-Transform Infrared Spectroscopy

pzc Point of Zero Charge

Acknowledgments

The author is thankful to Prof. Bart van der Bruggen of KU Leuven and Prof. Karoli Njau of Nelson Mandela African Institution of Science and Technology for their insightful comments during the writing of this manuscript.

Author Contributions

Hezron Timothy Mwakabona is the sole author. The author read and approved the final manuscript.

Funding

This work is supported by VLIR-OUS NSS project.

Conflicts of Interest

The author declares no conflicts of interest.

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Biography



Hezron Timothy Mwakabona is a Researcher at the Department of Applied and Earth Sciences at Mbeya University of Science and Technology. He completed his PhD in Chemical Engineering. For the past 10 years he has been researching the applicability of plant biomass in water defluoridation. He has also done several studies in metal corrosion and fluoride detection in water sources.

Research Field

Hezron Timothy Mwakabona: Water defluoridation; Metal corrosion; Fluoride detection